AD-A222 021

AD3762

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

[redacted] TION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

Development of New Ceramics for Novel Applications

5. TYPE OF REPORT & PERIOD COVERED

Final Technical Report

6. PERFORMING ORG. REPORT NUMBER

N/A

7. AUTHOR(s)

R. K. Mohr, D. Varshneya

8. CONTRACT OR GRANT NUMBER(s)

MDA-903-80-C-0470

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Catholic University of America
Vitreous State Lab, B2 Keane Hall
Washington, D. C. 20064

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

Defense Advanced Research Projects Agency
1400 Wilson Boulevard
Arlington, VA 22209

12. REPORT DATE

September 1982

13. NUMBER OF PAGES

50

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Same

OR

DTIC

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

High pressure sintering, ceramic materials (JG)
Nitrides,
Si_3N_4,

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The major objectives of this contract were (1) to establish a high pressure high temperature facility for the study of high performance ceramics and glasses and (2) to begin sintering studies of nitride materials. A high temperature high pressure apparatus was developed and tested to pressures of 30 KBar and 2150°C. This facility was used to sinter to 99% of theoretical density Si_3N_4 powders containing a few % of oxygen impurities

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

but no additives. In addition a glass was melted which contained 20 atomic percent nitrogen in the starting materials. Details of the furnace and properties of the sintered materials are reported.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

THE CATHOLIC UNIVERSITY OF AMERICA

Vitreous State Laboratory

Washington, D.C. 20064

FINAL REPORT

MDA-903-80-C-0470

Development of New Ceramics for Novel Applications

by

R. K. Mohr, Deepak Varshneya

Submitted to

Defense Advanced Research Projects Agency

October 1982

Table of Contents

Summary of Important Accomplishments

1. A high pressure, high temperature piston and cylinder apparatus was constructed and tested at pressures to 30 kbar at temperatures to 2150°C. This apparatus is designed to be used as a research tool for examining high temperature regions of the phase diagrams of nitrides, carbides and other refractory materials. High pressures are required at high temperatures to suppress decomposition or sublimation occurring in these materials at low or moderate pressures.
2. Relatively pure Si_3N_4 powders were sintered to 95%-99% of theoretical density without the addition of sintering aids. Sintering was examined at temperatures between 1600°C and 2150°C and pressures from 10 kbar to 30 kbar. The sintered samples were characterized according to crystal phase content, density, microhardness and microstructure. The temperature dependence of grain growth was examined and an activation energy was determined for this process to be 100 kcal/mole.
3. An oxynitride glass was made from starting materials having 20% Si, 20% La, 20% N and 40% O in atomic %. The sample was inhomogeneous but glassy in appearance. There was no evidence of foaming or appreciable reaction with the crucible.

I. INTRODUCTION

The high temperature, high strength ceramics, which include the nitrides, carbides and borides, will satisfy numerous important commercial and military applications if the problems of impurity-induced strength degradation and that of forming can be solved. Sufficient progress has been made in the past decade that German industrial research and development groups are promising a commercial ceramic gas automobile engine by 1990 and a Japanese company announced the successful testing of the world's first ceramic diesel engine in April of 1982.[1] While these reports are encouraging, the costs of component fabrication and property shortcomings suggest that significant developments must still be made before widespread application of the high performance ceramics will become a reality.

The processes contributing to the majority of successes with the high performance ceramics have been hot pressing, reaction bonding or high pressure gas sintering of single component materials such as Si_3N_4 or SiC. These are relatively expensive processes often requiring extensive post forming machining to obtain precision parts. In addition these processes require several percent of oxide impurities or other low melting temperature additives to overcome the "unsinterable" nature of the covalently bonded materials. While progress is being made in obtaining better sintering aids and lower impurity levels, it is generally accepted that the intergranular phase resulting from these necessary sintering aids and impurities is the cause of observed high temperature strength degradation and creep

phenomena. The answer to these problems may have to come from a different approach.

Many of the difficulties in forming useful shapes and in obtaining the ultimate properties of these materials would be overcome if they could be melted. The refractory nature of these materials and the fact that they decompose or sublime below their melting temperatures at atmospheric pressure has prevented the application of such a solution. By using high pressure, however, we can suppress decomposition and sublimation to examine normally inacessible temperature regions of the phase diagrams and sinter with a minimum of additives or determine melting temperatures if melting occurs. What we suggest is a systematic phase diagram study of the refractory ceramics at high temperatures, the ultimate goals of this approach being to find melting conditions for the single component materials or to find new eutectic compositions which provide lower temperature melting or sintering and the possibility of more conventional shaping techniques and yet superior properties.

Under this contract we have completed the necessary steps which give us the ability to do a systematic search for meltable compounds among the high performance ceramics. We have built and tested a piston and cylinder type high pressure furnace which will allow us to do sintering and melting studies at pressures sufficient to suppress decomposition and sublimation. In our initial work we have studied the sintering of relatively pure Si_3N_4 powders and have obtained densities of 99% of theoretical. We have also melted a high nitrogen content (20

atomic % by weight) glass in this apparatus. This is, of course, only the beginning of what should be done. What remains is to conduct the systematic phase diagram study we have suggested.

II. DEVELOPMENT OF NEW HIGH STRENGTH MATERIALS

A. Background

The nitrides and carbides, particularly Si_3N_4 and SiC, are currently of great interest because of their excellent properties at high temperature and stress. Because of their refractory nature and a tendency to decompose or sublime before sintering is achieved, efforts to fully sinter "pure" Si_3N_4, SiC or other high performance nitrides have had limited success. It has been necessary to employ densification aids to obtain dense compacted material. While these densification aids provide a means of obtaining useful materials, they also tend to compromise the properties expected from the pure materials. The densification aids, generally metal oxides and some nitrides in the case of Si_3N_4 and Si in the case of SiC, are materials that are or combine with the nitrides or carbides plus impurities to form an intergranular, viscous, liquid phase at sintering or hot pressing temperatures well below the melting or decomposition temperatures of the Si_3N_4 or SiC grains themselves. It is believed that densification is promoted through a solution reprecipitation mechanism.[2,3] Upon cooling, the liquid solidifies and forms secondary phases, which are in many cases glasses, although the distinction between glasses and crystals are blurred due to the small (10 - 50 A)[4] thickness of the phase. The composition of the glassy phase in commercial hot pressed Si_3N_4 (HS 110) has been determined by Kossowsky[5] to be 11 SiO_2:4.5 CaO:1 MgO:1 Al_2O_3 and in hot pressed SiC (NC 201 or NC 203) it has been determined by Kossowsky and Miller[6] to be an

aluminosilicate. At temperatures above 1100 - 1200°C these high silica oxide glasses begin to soften because of their relatively low glass transition temperatures, and, as noted, it is often their properties which ultimately control the failure of the composite.

To obtain materials having properties superior to existing ceramics will require new densification aids or new compositions which can be melted in pure form to obtain glasses or single crystal materials. There is a great deal of information in the literature on the thermo-mechanical properties of the nitrides indicating their superiority in many respects (density range, deformation temperature, elastic moduli, chemical durability and strength) to the silica-based oxide glasses forming the grain boundary phases of most present composites. It is not unreasonable to assume that a study of the phase diagrams of nitride crystalline materials would reveal the presence of eutectic compositions which would provide superior densification aids or new easily formed high performance glasses or single crystals.

B. Properties of High Performance Nitrides and SiC

We give here a very brief summary of the interesting properties of the high performance ceramics taken from several reviews.[7-12] Most of the property values reported here can be found in the Metals and Ceramics Information Center Report MCIC-HB-07 Vol. 1 concerning nitride properties.[12] By this summary, we intend to point out those properties of the nitrides and SiC which are exceptional, and, if obtainable in bulk material, would lead to significant commercial and military applications.

Perhaps the most obvious desirable property of these materials is their highly refractory character. The most studied of the nitrides, Si_3N_4, has not been melted but vaporizes or decomposes above approximately 1600°C in air. Boron nitride decomposes at about 2500°C while AlN has been melted at about 2700°C under 1500 psi nitrogen pressure. SiC decomposes or sublimes above 2600°C. While the refractory character of these materials is highly desirable the fact that most of them cannot be melted creates forming and densification problems which are currently the cause of failure to obtain the full potential of the materials.

Some of the nitrides and SiC have a high Young's modulus which suggests a potentially high strength. The Young's modulus of Si_3N_4 depends strongly on the method of formation. Reaction sintered forms have a Young's moduus greater than 21×10^6 psi which is equal to or greater than any of the oxide glasses while more dense hot pressed forms have a Young's modulus greater than 44×10^6 psi.[13] It is suggested that fully dense pure Si_3N_4 would have an even higher modulus. AlN has a Young's modulus of 50×10^6 psi while the values reported for single crystal SiC are as high as 85×10^6 psi.[9]

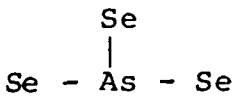
The range of densities for the nitrides is extremely wide, ranging from 2.5 to 16 g/cm^3. The highest density is more than 50% higher than one would expect to obtain with oxide glasses. Other properties of interest are specific heats, ranging from 0.05 to 0.5 Btu/lb°F with that for BN being the highest for all ceramics, and hardness as high as 3.3×10^3 kg/mm^2 for Si_3N_4 which is more than four times that for fused silica.

Although the bending strength of the nitrides and carbides at room temperature is not exceptional, it is limited primarily by the existence of surface and internal flaws. The strength of ceramics and all brittle materials suffers from the phenomenon of stress concentration at pre-existing flaws. Thus, ability to fabricate materials with minimal flaws is important in obtaining useful strength. An important property of the strength of these materials, however, is the fact that it does not degrade significantly at high temperatures. An examination of strength versus temperature for hot pressed Si_3N_4 indicates that the strength does not degrade until the glassy grain boundary phase begins to flow at about 1100 - 1200°C.[13] Reaction sintered Si_3N_4 maintains its strength, which is lower than hot pressed forms because of high porosity, well above these temperatures. Recently,[14] relatively pure Si_3N_4 has been densified at high pressure and temperature without additives. This material has superior high temperature hardness compared to Si_3N_4 densified with oxide additives. In addition, experiments on glass optical fibers coated with vapor deposited Si_3N_4[15] show no signs of stress corrosion in the presence of water vapor.

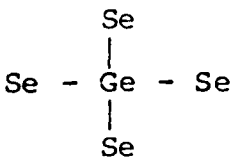
A major reason for the superiority of the nitride properties to those of many oxides is the increase in bond number afforded by nitrogen compared to oxygen. The replacement of oxygen having two bonds with nitrogen having three generally increases the density, hardness, modulus of rupture, chemical durability and the glass transition. This can be seen directly from the limited data on oxynitride glasses[16,17] where the above

property values increase linearly with nitrogen content or by analogy to other glass systems such as the chalcogenide glasses where more data is available.

For example, selenium glasses have each selenium atom bonded to two other selenium atoms -Se-Se-Se-. With the substitution of As we have structures of the form



which is a more dense structure and gives a higher glass transition temperature, T_g. T_g is further increased by the substitution of Ge with four bonds:



T_g and the moduli are increased as the percentage of As and Ge are increased.

Although a glass transition has not been observed in single component nitrides, there is reason to believe that glasses may exist and that they would have high T_g's. Amorphous Si_3N_4 has been formed by chemical vapor deposition. Whether this is a glass has not been determined. A recrystallization temperature of about 1400°C, however, has been observed. This would indicate a glass transition temperature near that value if it were to exist. If this were the T_g, it would be several hundred degrees higher than that of fused silica.

Further evidence for a high T_g is the general observation that T_g is approximately 2/3 T_m (melting temperature) for many single component glasses. When eutectics are found between high melting temperature compounds it is generally found that while T_m is lowered considerably the effect on T_g is much less dramatic. This explains why most commercial glasses are chosen to be near eutectic compositions, giving ease of forming while retaining the useful properties associated with a high T_g.

C. Basis for the High Pressure Studies

There is a severe lack of information on the phase diagrams of the high performance ceramics due to an inability to melt them at high temperature at atmospheric or moderate pressures. It is believed that a systematic study using high temperature, high pressure furnaces would offer the possibility of finding eutectic compositions among these compounds. The eutectic compounds should yield glasses, single crystal materials or superior densification aids depending on whether the viscosity is high, low or intermediate. Basic research should provide both better materials and a better understanding of the limitations on their use.

An ordinary phase diagram study of the nitrides is difficult or impossible due to their well-documented tendency to decompose or sublime at high temperatures. These tendencies must be suppressed if melting or sintering experiments are to be conducted on them. Reaction rate theory tells us that the rate of decomposition can be controlled by the ambient vapor pressures of the material components. Further, if thermodynamic

data is available for the material we can calculate the equilibrium vapor pressure as a function of temperature. When the components of the material are prevented from leaving the system or reacting with any other materials such as furnace elements, insulation, etc. and the equilibrium vapor pressures are equalled or exceeded then decomposition will be prevented.[18]

The JANAF Thermochemical Tables[19] contain the necessary thermodynamic data to make equilibrium vapor pressure calculations for Si_3N_4, one of the more important refractory ceramics. The reaction of interest is

$$Si_3N_4 \rightleftharpoons 3Si(l)+2N_2(v) \rightleftharpoons 3Si(v)+2N_2(v)$$

where (l) and (v) refer to the liquid and vapor forms respectively. One can first calculate the equilibrium vapor pressure for Si(v) from

$$P_{Si} = K_1 = e^{-\Delta G_{Si}/RT}$$

Where P_{Si} is the pressure referred to the reference state at one atmosphere, K_1 is the equilibrium constant. G is the free energy change for vaporization, R is the gas constant, and T is the absolute temperature. The equilibrium nitrogen pressure P_{N_2} can then be estimated from

$$(P_{Si})^3(PN_2)^2 = K_2 = e^{-\frac{\Delta G_{Si_3N_4} + 3\Delta G_{Si}}{RT}}$$

where K_2 is the equilibrium constant and G is the free energy of formation of Si_3N_4. Using these relations and the data from the

JANAF tables we have calculated the equilibrium nitrogen pressure. This pressure is plotted as a function of temperature in Figure 1.

The piston and cylinder pressure apparatus that we have used constitutes a sealed system. When the system is initially loaded and pressurized any void spaces existing in the furnace assembly and between particle grains was filled with air which is largely nitrogen thus the nitrogen partial pressure in the system was initially close to the applied pressure. A convenient minimum operating pressure for the apparatus is about 10 kbar. This pressure is sufficient to suppress decomposition for temperatures as high as 3000°C as can be seen from Fig. 1. This is true only if as mentioned above neither Si or N vapor are removed by chemical reaction with materials within the sealed furnace. We found that BN crucibles can be used successfully to prevent reaction or vapor transport so the melting studies we envision should be possible.

Once some of the melting temperatures are established it is likely that eutectic compounds having significantly lower melting temperatures will be found as has been the case for the silicates and other chemical systems. The discovery of such eutectic compounds should lead to one or more of three possibilities: (1) The viscosity of the melt will be high, favoring glass formation. (2) The viscosity will be intermediate, suggesting the probability of a superior densification aid. (3) The viscosity will be low, favoring the formation of single crystal materials. In all of these cases it should be possible to approach the superior properties indicated for the pure but difficult to form

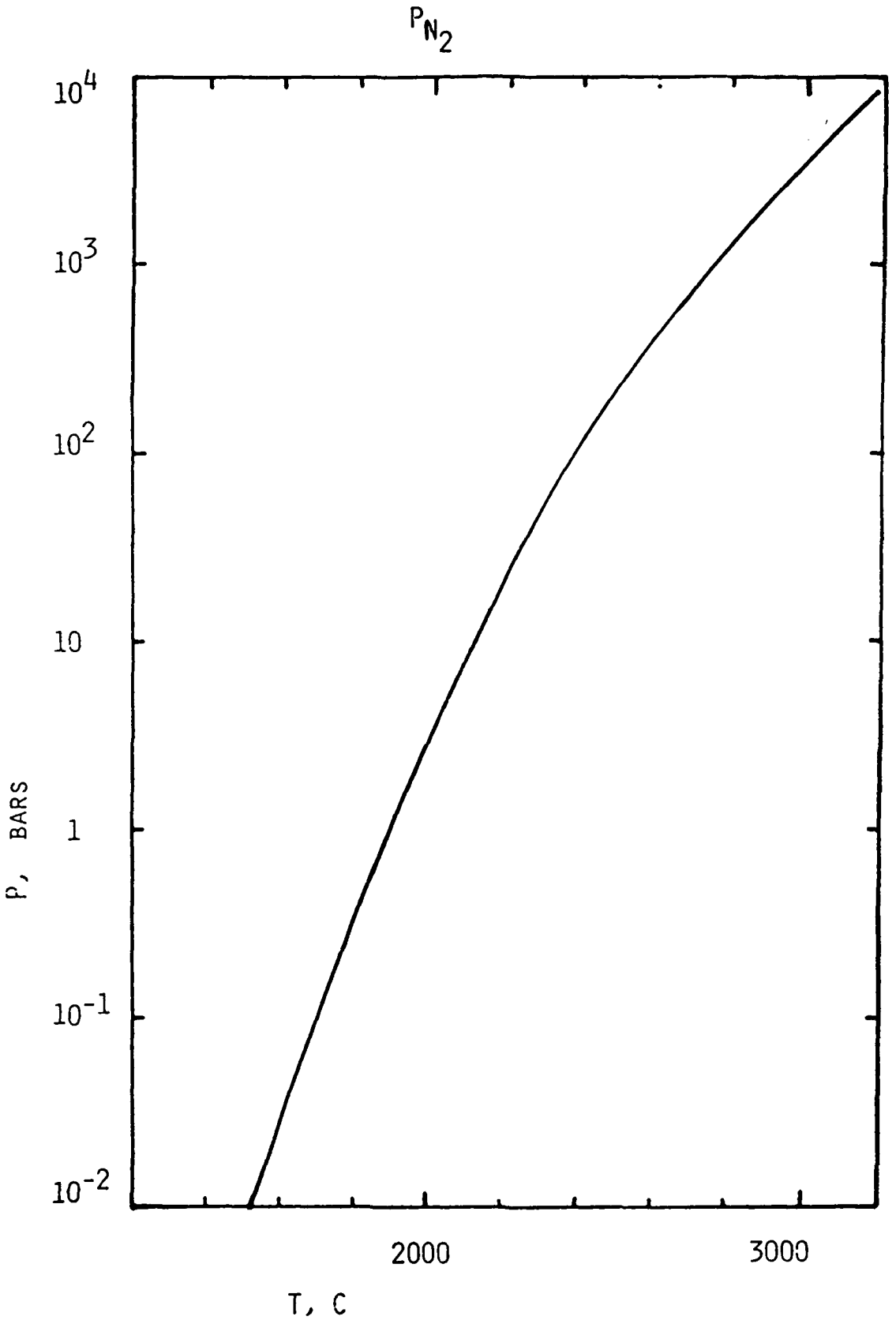


Figure 1. Nitrogen vapor pressure above Si_3N_4 as a function of temperature.

nitrides and SiC. It is the goal of this research to discover and characterize these new materials.

III. HIGH PRESSURE/TEMPERATURE APPARATUS

A. Introduction

The first task of this contract was to construct a high temperature, high pressure facility that would enable us to perform sintering experiments and melting point determinations for the nitrides and other refractory ceramics. High pressures are required as a means of suppressing the common tendency of these materials to decompose or sublime before their melting temperatures are reached. High temperatures are required because of the highly refractory nature of the high performance ceramics of interest. It is expected that useful compositions would have melting temperatures in the 2000 to 3000°C range. Fortunately, furnaces which can operate at high temperatures and pressures have already been developed,[20] primarily by geophysicists.

We selected a piston and cylinder type high pressure furnace for our work. Such furnaces have been used to more than 50 kbar and 3000°C. The Carnegie Institute Geophysics Laboratory in Washington, D.C. has been using such apparatus successfully for twenty years or more. Their staff was of considerable help in the design and construction of our pressure facility which adopts the design of Boyd and England.[21] We constructed the high pressure furnace and the associated pressure and temperature controls and used the facility to examine the sintering of relatively pure Si_3N_4 powders and a high nitrogen content glass. The facility was tested to 30 kbar and 2150°C during the course of this work. The details of the furnace are given below.

B. High Temperature High Pressure Furnace

The high pressure, high temperature apparatus that we built for our studies was based on the design of Boyd and England[21] which in turn was based on designs of Coes[22] and of Hall.[20] The basic design is relatively simple, incorporating a cylindrical tungsten carbide pressure vessel which is pre-stressed by steel support rings or "belts". Pressure is delivered by a cylindrical piston and is distributed approximately hydrostatically to the sample via crushable refractories. The heater consists of a graphite cylinder within and concentric with the pressure vessel. A large hydraulic press provides the end load against which the piston in the pressure vessel pushes.

A schematic diagram of the apparatus and the details of the furnace assembly are shown in Figures 2 and 3. In our apparatus we have used a 300-ton capacity hydraulic forming press for applying the end load. The press was a sheet metal forming press which we obtained as a surplus item through our DARPA contract. We redesigned the hydraulic system so that the original electric high volume hydraulic pump could be used for moving the 1000 pound platen to the approximate height to apply the end load to the bomb assembly. A manual auxilliary hydraulic pump was added so that the end load could be applied slowly and with adequate control. Gauges were also added so that a known end load could be applied.

The 300-ton press we obtained had platens which were 42 inches on a side and were much larger than required. Since the bomb assembly was only 7 inches in diameter, it was necessary to reinforce the platens with 3-inch thick soft steel plates covered

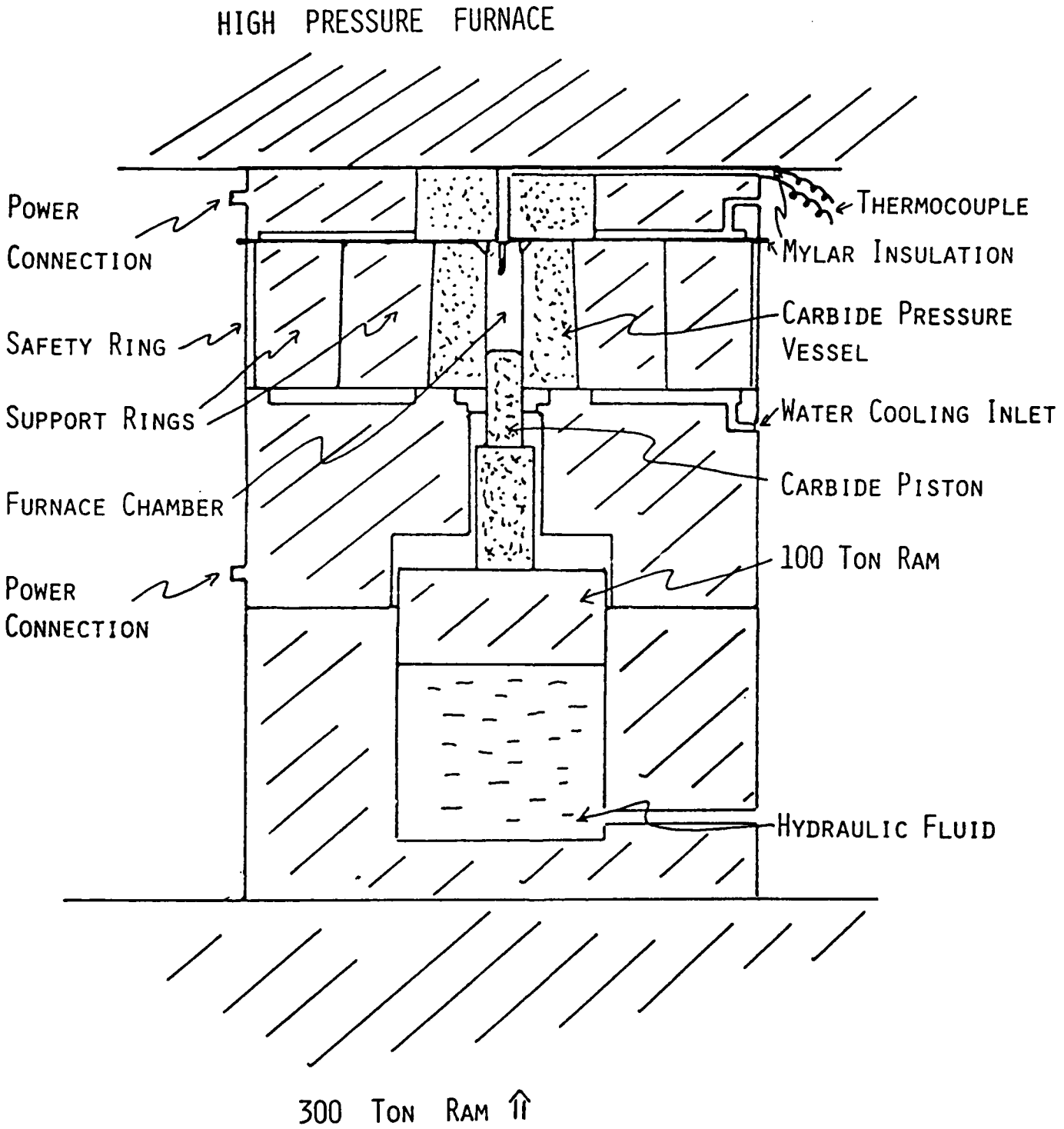

HIGH PRESSURE FURNACE
POWER CONNECTION
SAFETY RING
SUPPORT RINGS
FURNACE CHAMBER
POWER CONNECTION
THERMOCOUPLE
MYLAR INSULATION
CARBIDE PRESSURE VESSEL
WATER COOLING INLET
CARBIDE PISTON
100 TON RAM
HYDRAULIC FLUID
300 TON RAM

Figure 2.

FURNACE INSERT

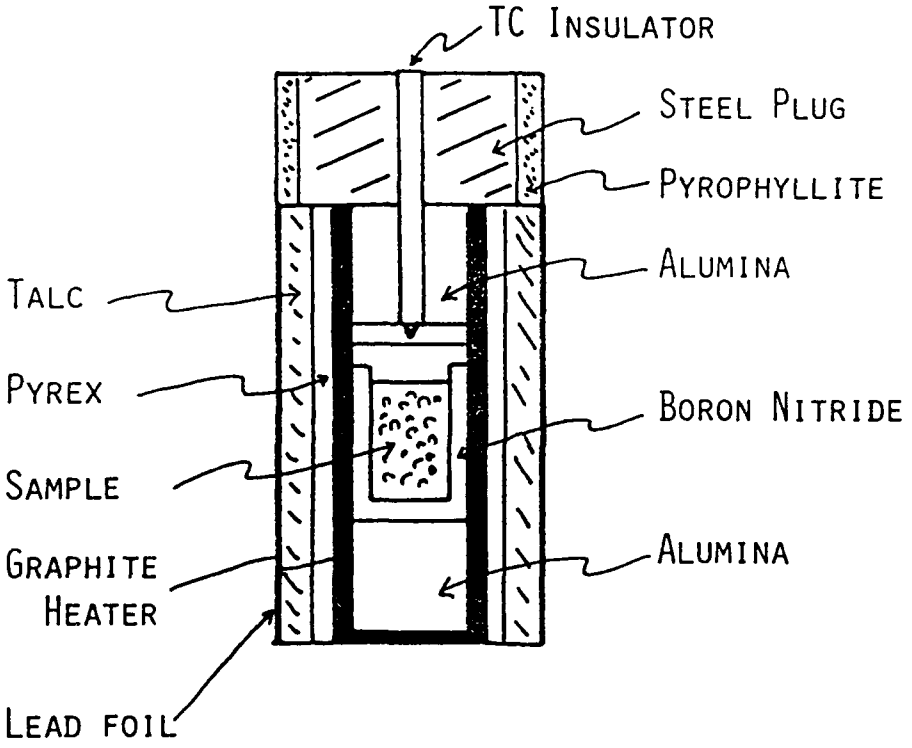


Figure 3.

by 1/2" thick hardened steel plates to spread the load over a large area of the platens which are of a ribbed cast semi-steel construction. The large size of the platens, though somewhat awkward, does allow the possibility of upscaling to a larger diameter pressure bomb which may be desirable in the future.

The pressure bomb assembly consists primarily of four parts. these include a top plate, a pressure plate, the bridge and a 100-ton ram with a carbide piston. The top plate consists of a steel ring surrounding a carbide disc. The plate has a groove on the top surface for a thermocouple insulator and the carbide disc has a hole through its center for passing the thermocouple and insulator. On the bottom of the plate a circular recess is machined which is connected to inlet and outlet holes for water cooling. A threaded hole is also provided in the side of the plate to attach one of the power leads for the heater. The top plate is electrically insulated from the press by a sheet of 0.013" thick mylar.

The pressure plate consists of several concentric rings. The outer ring is of soft iron and is a safety ring. The next two rings are of forged alloy steel which have been machined with a taper so that there is several thousandths of an inch interference in their fit. The core of the pressure plate is of tungsten carbide which has been machined with a taper on its outer surface and a 1/2-inch diameter bore. The tungsten carbide also has several thousandths of an inch of interference fit with the steel support rings. When the assembly is pressed together, the carbide core should be under approximately 10 kbar

of compression at room temperature. There is a bevel cut in the top of the bore of the carbide into which a matching pyrophyllite washer is placed to help in sealing the system and perhaps to prevent chipping of the carbide. The pressure plate is electrically insulated from the top plate by a 0.013" thick mylar sheet having a 1/2" diameter hole in its center to permit passage of the piston.

The bridge is a steel cylinder which contains a recess for cooling water in its top surface and inlet and outlet holes on the sides. The side also has a threaded hole for a power lead. The center portion of the bridge is bored out sufficiently to accomodate the half inch diameter carbide piston, a 1-inch diamter pusher piston and the 3-inch diameter ram. The bridge is constructed so that a 3/4-inch piston could be used in place of the 1/2-inch piston. This could be used with a pressure plate having a 3/4-inch bore which can be used to produce larger samples but of course has a lower pressure limit than the smaller system.

The ram has a 3-inch diameter cylinder and a load capacity of approximately 100 tons at a hydraulic pressure of approximately 23,000 psi. The hydraulic pressure was supplied by a handpump. The maximum pressure supplied by the 1/2-inch diameter piston is approximately 36 times that of the hydraulic fluid pressure or about 70 kilobar. The high temperature pressure limit for this apparatus is significantly lower than this pressure and is about 30 kbar or less depending on temperature.

C. Run Assembly

The details of the run assembly are shown in Figure 3. The assembly consists of a number of concentric cylindrical elements and several spacers. At the top of the run is a steel plug with a hole through its axis for the passage of the thermocouple insulator. The steel plug serves as the electrical lead for the top of the heater element. The plug is electrically insulated from the carbide bore of the pressure plate by a sleeve of pyrophyllite. The heater assembly consists of several concentric cylinders surrounding the sample region. The first cylinder serves as a lubricant for removal of the run and is made of lead or graphite foil approximately 3×10^{-3} inches thick. We found that the lead foil works well when the pressure plate is new; however, as the plate is used, cracks develop in the inner wall. The lead tends to melt during a run, filling these cracks and causing difficulties in removal. Graphite foil works well at all times, but is not commercially available in the desired thickness. We found that it could be thinned sufficiently by using a roller. This is time-consuming but is perhaps the best option currently available. The next cylinder is of talc which serves as a thermal insulator, an electrical insulator and as a pressure transmitter. The next cylinder is of Pyrex* glass which also serves as an insulator and, since it melts at the temperatures of interest, as a pressure transmitter. The Pyrex also serves to trap and hold any water released by the talc upon heating. The next cylinder is the graphite heater which can

---

* Corning Glass Works, Corning, NY.

either be machined from graphite rod or formed from graphite foil. A typical heater had a 0.25-inch inside diameter, a 0.030-inch wall thickness, a length of 1.25 inches and a resistance of 1.5×10^{-2} Ω. Failure of the heater element is one of the more frequent causes of a run failure. The most usual failure mechanism is rupture of the heater and loss of electrical continuity. This type of failure occurs if the various spacers and cylinders making up the heater assembly do not fit well allowing misalignment and nonsymmetric stresses on the heater. Poor fit and misalignment can also cause loss of or poor contact between the heater and the steel plug. These problems are particularly present when using a thin walled heater to maximize the available sample volume and to increase the heat input to the run assembly, as will be explained further in discussions of the temperature control of the furnace.

The region inside the heater cylinder has insulating spacers at the top and bottom which are made from a crushable alumina. The top spacer has a hole along its axis to pass the thermocouple insulator. The crushable refractory provides sufficient friction on the thermocouple insulator when pressure is applied that it prevents the extrusion of the thermocouple and insulator out of the furnace. Extrusion of the thermocouple and insulator if it occurs can cause a run failure by causing the thermocouple to break or to short out against the top plate of the assembly. Between the spacers is the crucible. We found that for Si_3N_4 α BN works very well as a crucible material. Its structure is similar to graphite, is easily machined and is a

good pressure transmitter. The crucible was shaped into a small cylindrical cup approximately 0.25 inches in diameter and 0.3 inches long. A cap was also machined to close the crucible. The BN is self-sealing when pressure is applied. BN has two very important properties for its use which are that it seems to provide a barrier to prevent vapor transport of Si and it does not seem to react with Si_3N_4 at the test temperatures. Earlier tests made with crucibles made of molybdenum and tantalum foils showed in both cases that the metals reacted with the materials around it even when protected with alumina sleeves. It was not possible to find any Si_3N_4 after the runs and it either reacted or decomposed. Any metal remaining was badly corroded.

D. Temperature Monitoring and Control

The thermal mass of the heater assembly is very small so the response time of the system is short. For good automatic temperature control, a very broad proportional band is required or alternately a system which controls a small fraction of the available power about a manually set equilibrium power. After initial unsuccessful attempts to use a Love model proportional temperature controller, we found that it would not satisfy the above requirements and the system oscillated uncontrollably. We found, however, that the system, although having a rapid response, was remarkably stable with time if the power input was stable. We were able to use manual control to obtain a temperature stability of better than ±5°C over a period of an hour, the time duration of most of our runs.

Power for the heater was supplied from a 208 volt line which was fed to a Sorenson model stabilizing step down transformer. The Sorenson transformer stepped the voltage down to 120 volts and supplied a variable autotransformer which in turn supplied the primary of a 10 to 1 high current step down transformer. The capacity of the system was 5 KVA at a final output voltage of 12 volts and slightly more than 400 amps.

The power that can be supplied to the system heater by this system is in practice limited by the resistance of the graphite heater. This is because of the 400 amp current limit of the final transformer. We found that heaters could be made with resistances ranging from about 1 to 3.5×10^{-2} Ω. The higher resistances are achieved by making the heater wall thinner. This procedure results in a weak heater and a high percentage of run failures. A second alternative is to use a transformer with a higher current capacity and much larger heater supply cables. The present system was adequate for obtaining temperatures of 2200°C. If higher temperatures are desired, some solution to the problem will be required.

In the temperature range which we operated (up to 2150°C) we could monitor the temperature with tungsten rhenium alloy thermocouples. These alloys are very brittle, especially after being heated to form the thermocouple bead. We used two different alloy thermocouple pairs, Tungsten-5 Rhenium versus Tungsten-26 Rhenium and Tungsten-3 Rhenium versus Tungsten-25 Rhenium. Although it is claimed that the second alloy is less brittle, we found no appreciable difference in their failure

rates for thermocouples welded using a tig welding method. The brittle nature of these thermocouples required that some care be taken in handling them to prevent weakening and subsequent failure during a run. These thermocouples are usable up to about 2300°C. Above those temperatures, although the thermocouple wires do not melt, it is difficult to find suitable insulators to hold the wires. If future experiments are to be done at higher temperatures, some other means of temperature determination than thermocouples will be required. One possibility is to estimate the temperature from the input power to the heater. Our observations of the power consumption as a function of temperature indicate that this will only provide a crude solution to this problem.

IV. SINTERING STUDIES

A. Introduction

The initial three quarters of the contract were consumed primarily by the construction of the high pressure, high temperature apparatus. In the remaining quarter, we chose to conduct a study of the sintering properties of Si_3N_4 with a minimum of impurities and no additives. The reasons for choosing this study were:

- Si_3N_4 is one of the most important of the high performance ceramics;
- Relatively pure starting powders are commercially available;
- We wished to examine a well-characterized material so that we could see if there were any significant differences in materials sintered with and-without significant additives;
- This study would be a good test of the capabilities of our system and would demonstrate the efficacy of using pressure to prevent decomposition at high temperatures;
- The scope of the study was such that it could be completed within the time remaining in the contract.

We examined the sintering of two Si_3N_4 powders, GTE SN 402 and SN 502, the first being largely amorphous and the second being more than 50% crystalline in form. The sintering characteristics of these materials were studied as a function of temperature and pressure. Some of the physical properties of the hot-pressed samples were then examined, namely density,

microhardness, crystalline phase content and microstructure size. We were also able to examine the temperature dependence of the grain growth in the microstructure and obtained an activation energy for the process.

Shortly after we began this study, an article was published by Yamada et al.[23] of work closely paralleling our own planned high pressure work and with the same starting materials. We decided to continue our work even though it duplicated in part work already published because we felt that the opportunity to compare results in a field new to us would be of value. In addition we planned to examine the sintering behavior under several conditions not reported.

B. Si_3N_4 Powder Selection and Treatment

There are a number of relatively pure Si_3N_4 powders available from different manufacturers. We obtained several samples and the manufacturers analysis of impurity content. From these we selected the GTE materials as having the smallest impurity levels among those powders which were available to us. There are difficulties in measuring impurity levels in these materials, especially the important oxygen impurity, so stated purity levels must be viewed with some caution. We do not presently have the capability to analyze the oxygen level in these materials in our laboratories so we were forced to rely on the manufacturers' values and on values reported in the literature of measurements made on different batches of the same type of material. In Table 1 we list the major impurities reported by the manufacturer and also list the oxygen contents measured

TABLE 1

Sample	Phase (wt%)		Contents of Elements (wt%)					
	α	β	N	O	Cl	Al	Ca	Fe	W
SN 502	56	4	38	0.8, 1.4*, 2.6**			0.02	0.002	0.00060.001 --
SN 402	Amorphous			35	1.4, 2.7*		3.66	0.002	0.00060.001 --
NC 132	--	--	--	2.5	--		0.21	--	0.432.5

* Reported by Yamada, Shimada & Koizumi[23]

** Reported by Prochazka and Greskovich.[3]

independently on different batches of the materials by other researchers. For comparison, we show the major impurity levels for a sample of NC 132, a commercial hot pressed material made by Norton Co. The sample contains similar or higher oxygen content but significantly more of other elements which act as sintering aids.

In addition to the chemical purity of the starting powders, it has been found that the particle size can have a strong effect on the sinterability of the material. SN 402 and SN 502 have specific surface areas of 19 and 3 m^2/gm respectively. Work by Greskovich[24] indicates that to achieve high density with covalent solids using conventional sintering one should start with particles having a specific surface area of approximately 23 m^2/gm or greater. Neither of the powders we chose to use satisfied this condition as received. Since we wished to determine if high pressures could overcome such sintering difficulties and because we did not wish to add contaminants to the powders we chose not to reduce the particle size before our sintering experiments.

The only pre-treatment given to the powders prior to sintering was to cold press them in a die to form a pellet which would fill the BN crucible. The cold pressing was done in a steel die at about 4 kbar. This yielded pellets with a density of approximately 50% of theoretical density or about 1.6 gm/cm^3.

C. Sintering Procedure

The details of a typical sintering procedure are given below. The cold pressed Si_3N_4 pellet is loaded into a BN crucible which is then closed with a BN cover. Since the BN is crushable, the crucible and cover become a well-sealed capsule surrounding the pellet when the apparatus is pressurized. The crucible and the other components of the furnace assembly are loaded into the pressure plate which is placed on top of the bridge plate. The 1/2 inch piston is advanced sufficiently that the steel plug at the top of the furnace assembly protrudes slightly from the pressure plate and through the hole in the mylar insulating sheet which is placed on top of the pressure plate. The top plate is then placed on the mylar sheet and the thermocouple hole in the top plate is lined up with the corresponding hole in the steel plug. The thermocouple and its insulator are then put in position with the tip of the thermocouple just touching the lid of the crucible. A sheet of insulating mylar is then placed on the top plate and the large press is closed and pressurized to provide an adequate end load (the larger of 100 tons or 1-1/2 times the runload). The small ram is then pressurized to about 10 kbar which is sufficient to seal the run assembly. Some cracking, normally from the Pyrex tube, may be heard during pressurization. It appears that the amount of compression on each side of the Pyrex tube and in fact on all parts of the run assembly are balanced well enough that distortion and run failure do not usually occur. The cooling water is then turned on to give a flow rate of approximately 2 gal/min. In some cases an auxilliary water cooling jacket of copper was

added around the pressure plate to prevent overheating, expansion of the support rings and resulting failure of the carbide core.

Heating was then begun with the temperature being raised at approximately 300°C/min. After reaching a temperature of 600°C to 700°C the pressure of the small ram was adjusted to give the desired run pressure. We then continued to raise the temperature to the desired final temperature and equilibrated the system. Equilibrium was usually reached in 5 to 10 minutes whereafter it was only necessary to make occasional adjustments to the heater power to maintain the temperature within a few degrees of that desired. During the course of the run to maintain the desired pressure it was necessary to make small adjustments in the small ram pressure to compensate for creep and other changes in the run components during heating.

The majority of our sintering experiments were conducted with a heating time of one hour measured from the time of reaching temperature equilibrium. After the desired heating time the power to the furnace was cut off. Under these conditions the estimated initial quenching rate for the sample is greater than 300°C/sec. When the power to the heater is cut, the pressure on the run decreases immediately due to cooling and shrinking of the piston. After several minutes the run and pressure plate reach room temperature and the cooling water is shut off and the apparatus is disassembled.

The run is removed from the pressure plate by pushing it out with a hydraulically driven piston. The insulators and the heater are then pealed from the crucible. The BN crucible is then chipped and ground away from the sample. The boundary between the BN and the Si_3N_4 is clearly visible indicating little if any reaction between the two materials. The sample normally had a well formed right circular cylindrical shape and was light to dark gray in color. Occasionally the sample was split in a plane perpendicular to the direction of the piston axis indicating that the pressure on the sample was not truly hydrostatic. The samples were then ground and polished using standard optical polishing techniques with cerium oxide or diamond being used as a final polishing material. The samples were then ready for evaluation of their density, microhardness, crystal phase content and microstructure.

D. Density Measurement

Hydrostatic weighing was used to determine the density of the samples after initial attempts to measure the density using a glass picnometer were abandoned because of the difficulty of obtaining consistent results with samples weighing approximately 0.5 g or less. We fashioned a small weighing basket of nichrome wire to hold the samples. The basket was then suspended from the weighing arm of a microbalance using 0.001 inch diameter wire. The small diameter of the wire decreased any effects of the miniscus formed at the wire-water interface. The samples were weighed in air and then in water. Care had to be taken to insure that air bubbles did not adhere to the samples or to the

weighing basket. With reasonable care the weight in air, W_A, could be reproduced within 50 μg and in water, W_W, within about 0.3 mg. The density of the sample, ρ, was then calculated from

$$\rho = \left(\frac{W_A}{W_A - W_W}\right) \rho_{H_2O}$$

where ρ_{H_2O} is the density of distilled water. The reproducibility of the density values was better than 0.5%.

The densities of several samples sintered at various temperatures and pressures are given in Table 2. These samples do not include the sample for which the largest density was obtained (ρ = 3.14) g/cc. This density was obtained in an aborted run which only lasted about fifteen minutes at about 1600°C.

Examination of the density data does not indicate any clear trends for our samples sintered for an hour at 1600°C or above. The majority of the densification must occur at times shorter than one hour at the pressures that we used (10-30 kbar). Yamada et al.[23] found in studies similar to ours that the majority of densification had been reached in 30 minutes or less. These observations were further confirmed by us by density measurements on several samples that resulted from runs that were aborted prior to one hour. In fact, as mentioned above, the highest density we observed was obtained in an aborted run lasting about 15 minutes. This behavior is to be expected and is explained qualitatively by Greskovitch et al.[24] The solution reprecipitation mechanism by which matter is transported in the

TABLE 2

Processing Temp. & Press. (SN 502)	Density g/cc.	Crystal Phases (α-β)	Micro-Hardness (GPa) (500g load)	Grain Size (μm) (length)
1600°C, 10kb	3.07±0.01	>90%β	16±1	2
1750°C, 10kb	3.05±0.01	>90%β	13±0.5	5
1900°C, 10kb	3.06±0.01	>90%β	12±1	8
2050°C, 10kb	3.08±0.01	>90%β	12±1	15
1600°C, 10kb	3.07±0.01	>90%β	16±1	2
1600°C, 20kb	3.08±0.01	---	---	<2
1600°C, 30kb	3.13±0.01	---	---	<2
2100°C, 30kb	3.06±0.02	---	---	3-4
2150°C, 10kb (SN 402)	3.01±0.01	>90%β	11±0.5(385g)	10-15
Norton Si_3N_4 (NC 132)	3.25±0.01	---	17.5±0.5	---
Alumina	3.97	---	18	---
Diamond	2-2.5	---	80	---

[12], 1281 (1981).

nitrides at high temperatures and in the presence of even small amounts of oxide liquid tend to promote grain growth rather than rearrangement of the grains and/or coallescence. The formation and growth of grains with a high aspect ratio impedes the densification process and it is claimed that if high density is to be obtained it must be complete before grains with high aspect ratio are formed.

E. Microhardness Measurements

Microhardness measurements were made on the samples using a Leitz Miniload hardness tester. The samples were mounted in Bakelite using a mounting press and were polished using diamond or cerium oxide abrasives. Diamond indents were made using a Vicker's diamond indentor using loads ranging from 50 g to 1 kg. The indentor load was applied for ~20 seconds. After several indents were made the indent size was measured and the microhardness calculated acording to the formula

$$\text{Microhardness(MPa)} = \frac{9.8 \times 1854 \times \text{load(g)}}{(\text{indent length}(\mu\text{m}))^2}$$

The microhardness exhibited a load dependence with the hardness value decreasing with increasing load until an apparent saturation was reached at a load of 500 g. The observed scattered in the hardness values also decreased somewhat with load. At higher loads, cracking began to appear at the corners of the indent making the readings suspect. For these reasons the results obtained with a 500 g load were judged to be the most reliable and the measured values for several samples are

reported in Table 2. The only trend indicated by this limited data was that the hardness seems to decrease with increasing sintering temperature. The microstructures examination discussed below indicates that the higher sintering temperature results in increased grain size and may be responsible for this feature.

F. Crystal Phase Content

The crystal phase content of the sintered samples was determined by x-ray diffraction using graphite filtered Cu Kα radiation. The weight fractions of the phases, α or β, were estimated using the ASTM 9-250 for the α phase and the ASTM 9-259 for the β phase. The small size of the samples limited the accuracy of these estimates to about ±10%. The results of the measurements are given in Table 2. The results indicate that the conversion of the α phase to the β phase was complete within our detection limits for all samples examined.

G. Microstructure

Scanning electron microscopy was used to examine the Si_3N_4 starting powders and the development of microstructure of the processed samples as a function of both the sintering pressure and temperature. The secondary electron image was used primarily which gives topographical information on the surfaces examined. Polished surfaces of the samples revealed little image contrast so etching of the surfaces was required. An etch of 40% HF and 20% HNO_3 in an aqueous solution for 10 to 12 minutes at room temperature was used. A typical micrograph of an etched area within an indent is shown in Figure 4.

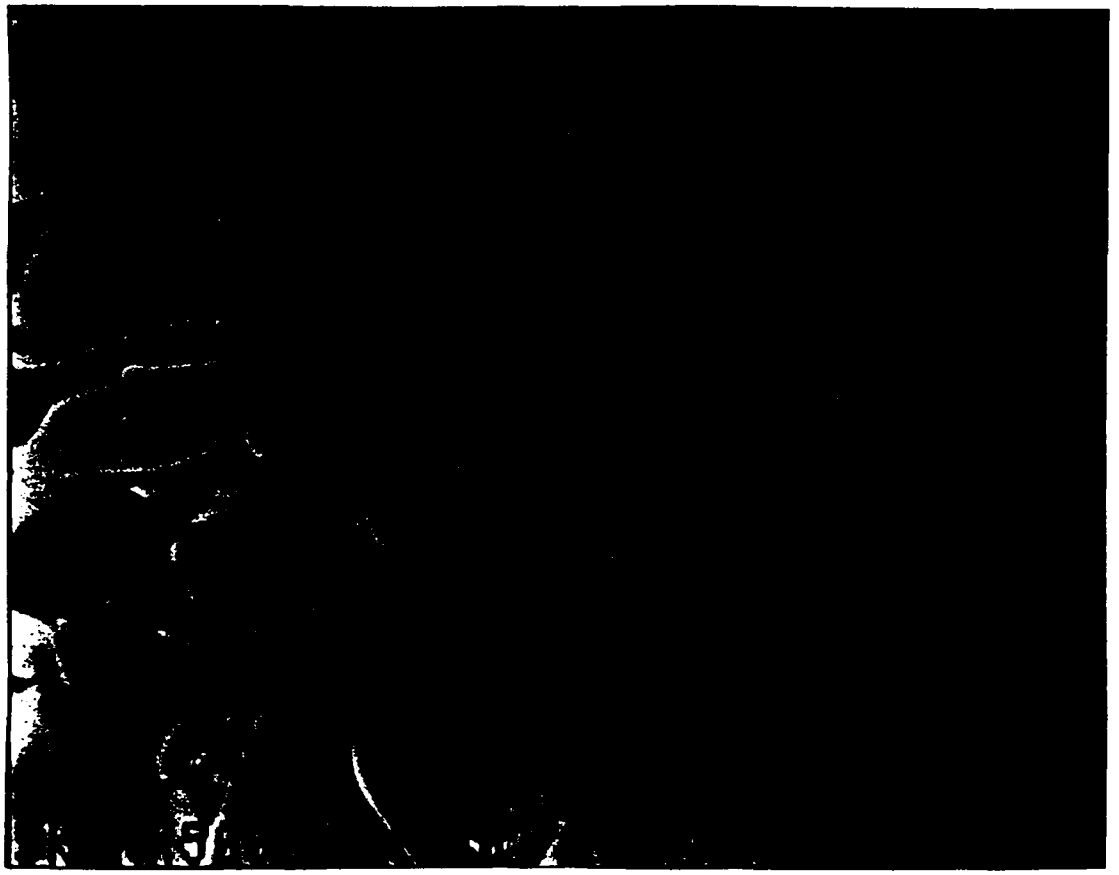


Figure 4. Micrograph of an etched area within an indent in Si_3N_4

Examination of the SN 502 starting powder showed a mixture of thin needle-like particles with clusters of roughly spherical particles with each occupying approximately equal volume. The needles were approximately 10 μm in length and 0.1 μm to 1 μm in width. The spherical particles were approximately 1 μm in diameter. This is consistent with the manufacturer's estimate of an average particle size of 0.7 μm. Different particle structures were to be expected since the powder was a mixture of α and β crystalline phases and of amorphous material.

Samples were examined that had been sintered at 1600°C for one hour at 10, 20 and 30 kbar. The SEM images of these samples after they had been polished and etched as described above revealed that the etching was progressively less effective on the samples as a function of increasing sintering pressure. The surface of the sample sintered at 30 kbar showed only scattered etch pits on the surface. This observation is consistent with the fact that the sample prepared at higher pressure had a higher density and thus fewer voids than that sintered at lower pressure.

The microstructure size of a set of SN-502 samples sintered at a pressure of 10 kbar for one hour at temperatures of 1600, 1750, 1900 and 2050°C was determined from etched regions of the sintered samples. The average microstructure volume was estimated from the average length and cross sectional diameter of the elongated hexagonal grains of the samples. Typical micrographs of each sample taken at a magnification of 3000 are shown in Figure 5. The increase in microstructure size with

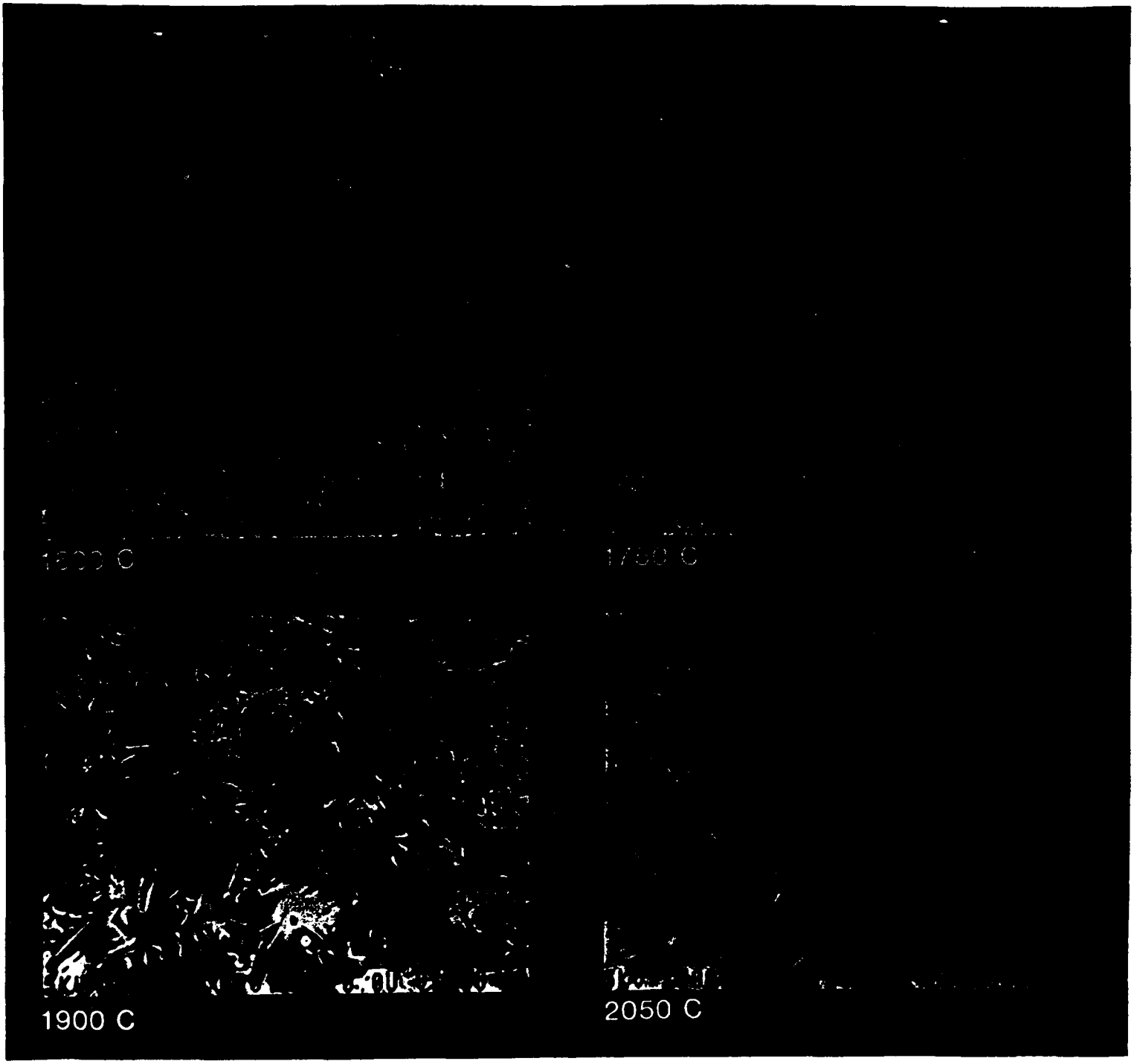


Figure 5. Micrographs of Si_3N_4 samples sintered at 1600 C, 1750 C, 1900 C and 2050 C for 1 hour at 10 kbar showing the effect of sintering temperature on microstructure size.

temperature is clearly visible from these micrographs. We attempted to quantify this observation by measuring the dimensions of large numbers of grains and finding the average volume calculated from these dimensions as a function of sintering temperature. The uncertainty in these measurements is large because of the significant range of particle sizes found at all temperatures and because it was difficult to find many grains which had their entire lengths exposed. This would tend to discriminate against the measurement of long grains. In particular, one would expect the estimate of particle volume to err increasingly as the average grain length increased, i.e. as the sintering temperature increased. Even with these problems one would estimate the accuracy of the volume determinations to be better than 25% and since the observed volume change was more than two orders of magnitude it seemed reasonable that one might try to estimate an activation energy for the grain growth process.

Figure 6 shows an Arrhenius plot of grain volume versus temperature. From this we obtain an activation energy for grain growth of approximately 100 kcal/mole. This is approximately the same activation energy measured for the $\alpha \rightarrow \beta$ phase transformation measured in Si_3N_4 sintered with[2] and without[23] significant additives. This would suggest that the mechanism responsible for the transport of material resulting in the phase transformation may be the same as that responsible for grain growth. The mechanism most commonly reported for these processes is that of solution reprecipitation. The liquid phase involved is

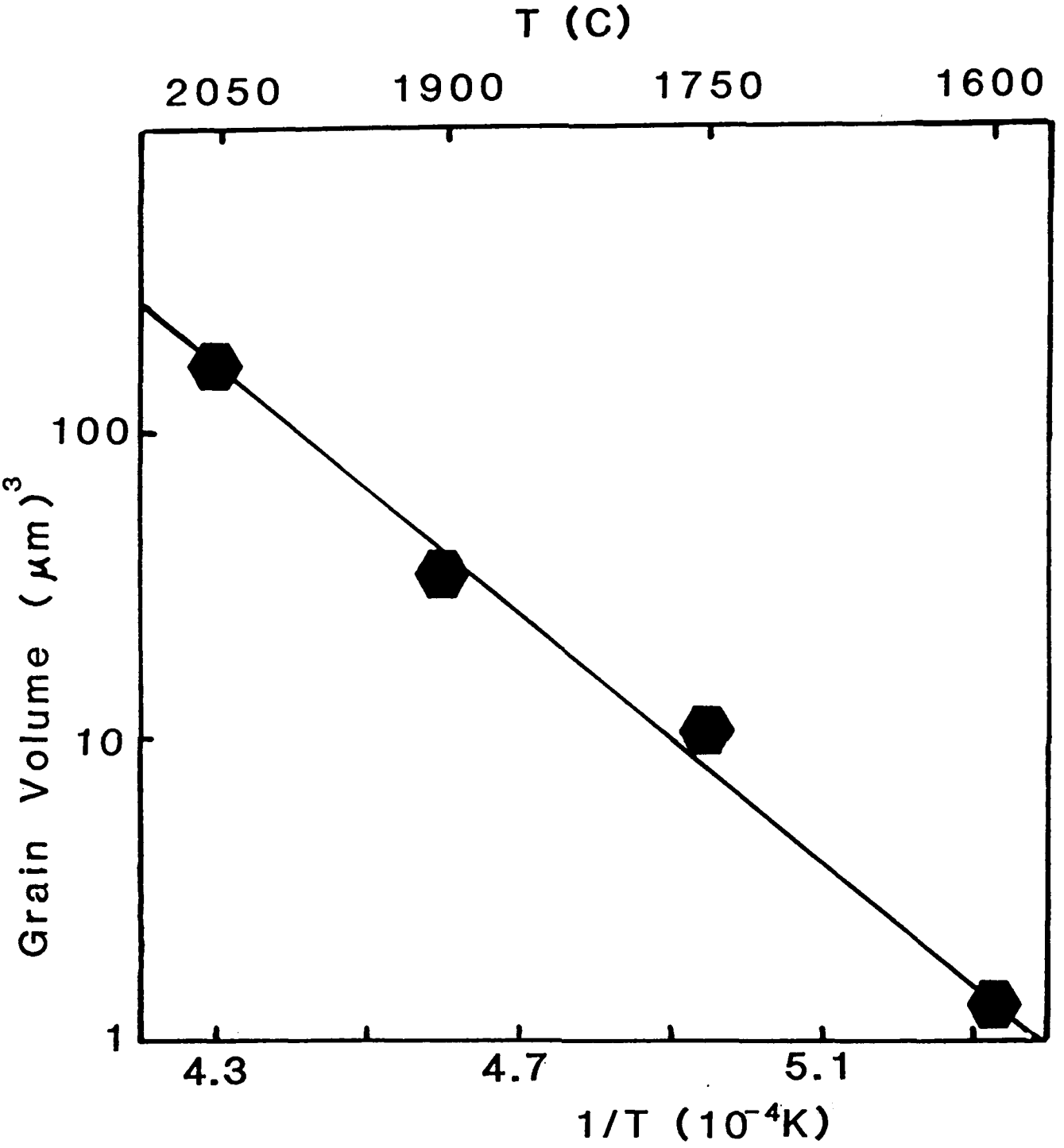


Figure 6. An Arrhenius plot of grain volume in Si_3N_4 sintered for 1 hour at 10 kbar.

largely oxide in composition. Although no additions were made to the starting materials, significant impurities apparently exist as indicated by etching of a low durability material (presumably an oxide) between the Si_3N_4 grains in the sintered samples and as indicated in the reported chemical analysis of the starting powders. The densification that we have observed in our experiments is apparently similar in nature to that observed with nitrides containing significant additives. The use of high pressure, however, does seem to help promote densification, prevent substantial decomposition and decrease the additive requirements for densification.

Samples prepared from SN 402 which is an amorphous starting material did not show good densification below temperatures of 2150°C. Examination of the microstructure showed the same elongated hexagonal crystals as in the sintered SN 502 material. This would indicate that the amorphous phase had been converted mostly to the β phase during sintering. This is in agreement with the x-ray data. The difficulties in densifying the amorphous material has been reported by other researchers.[23,25] It is possible that the high chlorine content of the starting materials may retard densification. It has been reported that Cl retards the α to β phase transformation.[26]

H. Oxynitride Glass Fabrication

To examine the feasibility of melting high nitrogen content oxynitride glasses in our high pressure apparatus we attempted to melt a composition having the highest nitrogen content reported in the literature.[27] This was a glass with 20% La, 20%

Si, 20% N and 40% O by atomic %. The starting powders were La_2O_3, Si_3N_4 and SiO_2 mixed in the appropriate ratio. Mixing was accomplished by dry milling the powders. After mixing, the powders were treated in the same fashion described above for Si_3N_4 sintering. The cold pressed pellet was heated for one hour at 1700°C under 10 kbar of pressure.

The resulting sample was only examined qualitatively. The sample had formed into two slightly flattened spheres which were smooth and glassy in appearance but were inhomogeneous in color. There was no evidence of foaming or of significant interaction with the BN crucible. Our conclusion is that this method would be useful in melting new compounds of high nitrogen content but the additional work will be required before full value of the procedure can be adequately appraised.

I. Summary and Conclusions

We constructed and tested a high pressure high temperature facility which will serve as a useful research tool in studying the sintering and melting of refractory materials. This facility will be particularly useful in studying materials which show a tendency to decompose and/or sublime at high temperatures at atmospheric pressures such as the nitrides. Using this facility we initiated preliminary studies of the sintering characteristics of Si_3N_4 without additives and melted an oxynitride glass. We were able to obtain densities in Si_3N_4 near theoretical even without additives using high pressure sintering; however, we saw no evidence of melting at temperatures to 2150°C. The sintering behavior appears to be similar to that observed in conventional

hot pressing using additives. It is thought that oxide additives and/or oxide impurities provide a liquid at high temperatures which promotes densification via a solution reprecipitation mechanism. The use of high pressures appears to reduce the amount of liquid required but the liquid still appears to play an important role in the material transport process. This is suggested by the fact that grain growth and the $\alpha \rightarrow \beta$ transition have approximately the same activation energy in Si_3N_4 sintered with and without additives implying that the same material transport mechanism dominates even with relatively low impurity content.

References

1. James I. Mueller, Am. Ceram. Soc. Bull. 61, 588 (1982).

2. R. Raj and P. E. D. Morgan, Comm. Am. Ceram. Soc., C143 (1981).

3. S. Prochazka and C. D. Greskovich, Report # AMMRCTR 76-32, Nat. Tech. Inf. Ser. (1978).

4. O. L. Krivanek, T. M. Shaw and G. Thomas, J. Am. Ceram. Soc. 62, [11-12], 585 (1979).

5. K. Kossowsky, J. Mat. Sci. 8, 1603 (1973).

6. K. Kossowsky and D. G. Miller, Basic Sci. Div. meeting of the Am. Ceram. Soc., Pittsburgh (Sept. 1973).

7. W. J. Croft and I. B. Cutler, Powd. Met. Int. 6, 92 (1974).

8. F. F. Lange, Annual Rev. of Mat. Sc. 4, 365 (1974).

9. D. J. Godfrey, Proc. Brit. Ceram. Soc. 22, 1 (1973).

10. "Ceramics for High Performance Applications", ed. by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill Publishing Co., Chestnut Hill, Mass., 1974).

11. "Ceramics for High Performance Applications II", ed. by J. J. Burke, E. N. Lenoe and R. N. Katz (Brook Hill Publishing Co., Chestnut Hill, Mass., 1978).

12. "Engineering Property Data on Selected Ceramics Vo. I, Nitrides" report MCIC-HB-07 Vol. I, Metals and Ceramics Information Center, Battelle-Columbus Laboratories, Columbus, Ohio (1976).

13. J. W. Edington, D. J. Rowcliffe and J. L. Henshall, Powd. Met. Int. part I 7, 82-96 (1975); part II 7, 136-147 (1975).

14. K. Tsukuma, M. Shimada, and M. Kuizumi, Am. Ceram. Soc. Bull., 60 (9), 910 (1981).

15. R. Hiskes, Digest of the Topical Meeting on Optical Fiber Communications, Washington, D. C. (1979) paper WF6.

16. R. E. Loehman, "Preparation and Properties of Yttrium-Silica-Aluminum Oxynitride Glasses", to be published by the American Ceramic Society.

17. T. H. Elmer and M. E. Nordberg, Proc. VII Int. Cong. on Glass, Brussels, Belgium, 1965, Institut National de Verre, Charleroi, Belgium, 1965.

18. G. Greskovich and S. Prochazka, Comm. Am. Ceram. Soc. C-96 (1981).

19. D. R. Stull and H. Prophet JANAF Thermochemical Tables 2d ed. NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C. 1971.

20. H. T. Hall, Rev. Sci. Inst. 29 (4) 267 (1958).

21. G. R. Boyd and J. L. England, J. Geophysical Res. 65, 741-748 (1960).

22. L. Coes, J. Am. Ceram. Soc. 38, 298 (1955).

23. T. Yamada, M. Shimada and M. Koizumi, Am. Ceram. Soc. Bull. 60,

24. C. Greskovitch and J. H. Rosolowski, J. Am. Ceram. Soc. 59, [7-8], 336 (1976).

25. M. Shimada, N. Ogawa, M. Koizumi, F. Dachille and R. Roy, Am. Ceram. Soc. Bull. 58, [5], 519 (1979).

26. D. R. Clarke, Comm. Am. Ceram. Soc. C21 (1982).

27. A. Makishima, M. Mitomo, H. Tanaka and M. Tsutsumi Yogyo-Koykai-Shi 88 [11], 701 (1980).